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Hemicellulose Composition of Dietary Fiber of Milled Rice and Rice Bran

Robert R. Mod,* Edith J. Conkerton, Robert L. Ory, and Floyd L. Normand

Water- and alkali-soluble hemicelluloses from milled rice and alkali-soluble hemicellulose from the bran were isolated, purified, and characterized. The ratios of arabinose to xylose for the four alkali-soluble rice bran and endosperm hemicelluloses were 1.1:1, 0.9:1, 0.9:1, and 0.8:1, 1.3:1, 1.3:1, 1.8:1, and 1:1; and for the water-soluble hemicelluloses, 4:1, 6:1, 7:1, and 7:1. Amino acid patterns for the proteins associated with hemicelluloses indicate that they are atypical of plant proteins. The water-soluble hemicelluloses contain significant amounts of hydroxyproline. Disc gel electrophoresis of one alkali-soluble rice bran hemicellulose suggests that the proteins are chemically bound to the carbohydrate. The range of crude and neutral detergent fiber contents of rice brans was 9.2 to 21.1% and 29.7 to 44.7%, respectively.

As the first phase of investigations on the role of nonstarch carbohydrates of rice, we are examining the qualitative and quantitative differences between the hemicelluloses of rice from different growing areas. Hemicelluloses, along with cellulose, lignin, and pectin, are major constituents of the cell walls of cereal grains, seeds, fruits, and vegetables and, collectively, they are part of the dietary (food) fiber. Dietary fiber of plant foods, especially cereals, is currently receiving much attention as an essential nutrient that has beneficial effects on hypercholesterolemia and various intestinal disorders (Scala, 1976). All of these nonstarch carbohydrates have a unique stability property; they are relatively unchanged by cooking and they are not readily digested by secretions of the human digestive system when eaten (Scala, 1975). Dietary fiber is the general term given to the plant material that is not digested by human digestive enzymes. It is not the same as crude fiber, and its concentration in foods is always higher than that of the crude fiber content (the insoluble residue after sequential extraction of the material with solvent, dilute acid, and dilute alkali). Analysis of crude fiber content may remove 80% of the hemicellulose and 50–90% of the lignin before the residue is estimated (Van Soest and McQueen, 1973). Thus, crude fiber values listed in proximate analyses are not indicative of the hemicellulose content of foods.

Unlike other fiber constituents such as pectins, cellulose, or lignins, hemicellulose is not composed of only one or two components, but is a complex material containing several hexoses, pentoses, hexuronic acids, and amino acids with different functional groups that are potentially capable of reacting with other components during cooking and digestion. The composition and structure of wheat-flour hemicellulose (pentosans) have been extensively investigated (Neukom et al., 1967, 1975; Cole, 1967; Medcalf et al., 1968; Fincher et al., 1974). Rice hemicelluloses have received relatively little attention (Matsuo and Nanba, 1958; Gremli and Juliano, 1970; Cartaño and Juliano, 1970; Bevenue and Williams, 1956). All of these investigators found glucose, arabinose, xylose, and galactose in this rice polysaccharide. Mannose was also detected, but only after extraction with 24% KOH (Bevenue and Williams, 1956) or after partial enzymatic removal of the main sugar constituent (Gremli and Juliano, 1970). A proteoglycan (hemicellulose) that contained rhamnose, xylose, arabinose, glucose, galactose, and 17 amino acids was isolated by hot water extraction from rice bran (Yamagishi et al., 1975) and was found to contain *O*-α-L-arabinofuranosylhydroxyproline (Yamagishi et al., 1976).

Wheat bran has received much more attention from nutritionists than has rice, but there are differing opinions

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Table I. Composition of Alkali-Soluble, Rice-Bran Hemicelluloses

variety	composition (weight %)								
	Rham	Ara	Xyl	Mann	Gal	Glu	protein, N × 5.95	uronic acid	Ara/Xyl ratio
Starbonnet									
La.	2.6	34	30	tr	5	4	9.58	10	1.1/1
Ark.	2.0	24	27	0.9	10	tr	15.89	12	0.9/1
Tex.	1.7	24	32	1.0	9	2	18.45	12	0.8/1
Calrose (Cal.)	1.3	22	29	0.7	8	4	26.42	9	0.8/1

on their contents. One anonymous report (Food Product Development, 1976) mentioned 9% fiber in wheat bran and 7–8% in rice bran; another article (Goe, 1976) mentioned 9% for wheat bran and 12% for rice bran. Not all people can tolerate whole wheat bran (Painter et al., 1972); however, there should be no problem with rice bran because rice is considered to be more digestible and less irritable to the intestinal wall than is wheat bran; e.g., defatted rice bran has been used in baby foods for many years.

This report describes the extraction and purification of the water- and alkali-soluble hemicelluloses from the endosperm and the alkali-soluble hemicellulose from the bran of two varieties of rice grown in four areas. Their sugars, hexuronic acid and amino acid compositions, and the contents of their crude and neutral detergent fibers are compared.

MATERIALS AND METHODS

Samples of long grain Starbonnet rice from Crowley, Louisiana; Beaumont, Texas; and Stuttgart, Arkansas, and of medium grain Calrose from California, Nato and Brazos from Texas were dehulled in a McGill sheller and milled in a McGill miller No. 3 for 1 min. A 2-lb load was used for the long grain rice and a 7-lb load for the medium grain rice for the first 30 s; no load was used for the remaining 30 s. The milled rice was ground to pass through a 20-mesh screen, placed in a Soxhlet extractor, and extracted with hexane for 3 h to defat the milled rice. After air drying, the defatted rice was ground to a fine powder in a ball mill. The rice bran was defatted with hexane as previously described.

Water- and alkali-soluble hemicelluloses from milled rice were isolated by a slight modification of the procedure of Cartano and Juliano (1970). Mycolase (mixed amylases) was used in place of α-amylase to degrade the large amount of starch from the alkali-soluble hemicelluloses. The water-soluble, hemicellulose-free residue was heated with an equal volume of distilled water to gelatinize the starch and cooled to 40 °C. Mycolase in pH 7 phosphate buffer was added along with a few drops of toluene, and the mixture was stirred for 24 h at 40 °C and then centrifuged. Additional mycolase, distilled water, and toluene were added to the residue, after which the mixture was stirred for 10 days at 40 °C, with centrifugation taking place at 24-h intervals. After isolation and purification, the water- and alkali-soluble hemicelluloses were obtained in 0.02 and 0.13% yields, respectively. Alkali-soluble hemicellulose was isolated from the bran by the procedure of Gremli and Juliano (1970) in 1.3% yield.

The hydrolyzed sugars were identified qualitatively and quantitatively by gas chromatographic (GC) analysis on a Hewlett-Packard Model 5750 equipped with a flame ionization detector. The column used was a stainless steel tube, $^1/_8$ in. o.d. 10-ft long, packed with 5.8% OV-1 on Chromosorb W, 60–80 mesh. The column was operated isothermally at 190 °C with a carrier gas flow of 18 mL/min. The sugars were equilibrated overnight in pyridine and silylated with trimethylchlorosilane and hexamethyldisilazane according to the procedure of Sweely et al. (1963). The equilibrated and silylated sugars were identified by comparing their retention times and peak enhancement with known sugars. Quantitative estimates of each sugar present were made by comparison of peak areas with that of sorbitol as an internal standard.

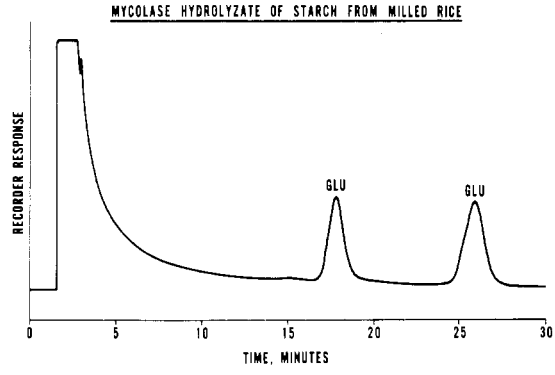

Figure 1. GC curve of enzymatic hydrolyzate of starch from milled rice; GLU, glucose.

Polysaccharides were hydrolyzed by the procedure of Roberts et al. (1976). Nitrogen was determined by micro-Kjeldahl, protein as nitrogen × 5.95 and hexuronic acid by the procedure of Wardi et al. (1974). High-voltage paper electrophoresis was done in 0.05 M borate buffer at pH 9.2, and 10 × 20 cm glass plates coated with 0.25 mm of silica gel without gypsum were used for thin-layer chromatography. After three successive ascending developments in chloroform–methanol (60:40), color was developed with α-naphthoresorcinol sulfuric acid according to Patuska (1961). Polyacrylamide gel electrophoresis was by the procedure of Davis (1964), and amino acid composition was determined according to Conkerton (1973) and Kaiser (1974).

RESULTS AND DISCUSSION

Before beginning any GC analyses of the sugars isolated from the various hemicelluloses, it was necessary to determine if the mycolase preparation had any hemicellulase activity. The starch hydrolyzate was analyzed after mycolase treatment. The GC curves in Figure 1 show two peaks for glucose only, suggesting that the hemicellulose is probably not hydrolyzed during starch removal.

The composition of the alkali-soluble, rice bran hemicelluloses is shown in Table I. All of the rice varieties contained the same sugars—rhamnose, arabinose, xylose, mannose, galactose, and glucose. Since rhamnose and mannose in rice hemicellulose had not been reported previously, thin-layer chromatography was used to verify their presence. By this method rhamnose was found but not mannose, which may have been hidden by glucose. For additional proof, high-voltage paper electrophoresis was then used to analyze these samples, and the presence of both rhamnose and mannose was confirmed. Although these alkali-soluble rice bran hemicelluloses contain higher amounts of arabinose and xylose than are found in any of the other hemicelluloses, they also contain the lowest

Table II. Composition of Alkali-Soluble, Rice Endosperm Hemicelluloses

variety	composition (weight %) Rham	Ara	Xyl	Mann	Gal	Glu	protein, N × 5.95	uronic acid	Ara/Xyl ratio
Starbonnet									
La.	1.1	32	24	1	5	18	9.46	10	1.3/1
Ark.	3.0	13	10	3	5	18	27.91	10	1.3/1
Tex.	1.2	22	12	10	3	15	26.78	10	1.8/1
Calrose (Cal.)	3.0	17	17	3	6	34	10.83	10	1/1

Table III. Composition of Water-Soluble, Rice-Endosperm Hemicelluloses

variety	composition (weight %) Rham	Ara	Xyl	Mann	Gal	Glu	protein, N × 5.95	uronic acid	Ara/Xyl ratio	Ara/Gal
Starbonnet										
La.	0.7	8.3	2.4	0.7	11.0	51	3.09	6	4/1	0.8/1
Ark.	0.6	9.0	1.4	8.4	11.9	47	2.38	8	6/1	0.8/1
Tex.	1.0	7.4	1.1	1.6	11.8	54	3.57	9	7/1	0.6/1
Calrose (Cal.)	0.7	3.4	0.5	3.4	5.0	55	1.67	9	7/1	0.7/1

amounts of glucose. With the exception of Starbonnet-La., in which arabinose was the predominant sugar, the remaining samples showed xylose as the predominant sugar. Similarly, the ratio of arabinose to xylose for Starbonnet-La. was 1.1:1, whereas that for the remaining Starbonnets and Calrose was less than 1:1 (about 0.8:1). These ratios are the lowest found for any of the hemicelluloses investigated.

The amounts of protein associated with these polysaccharides were not uniform and ranged from a low of 9.6% for the Starbonnet-La. to a high of 26.4% for the Calrose. The hexuronic acid contents, which ranged from 9 to 12%, were higher than for any other hemicellulose analyzed.

The composition of the alkali-soluble rice endosperm hemicelluloses is shown in Table II. All of the varieties contained the same sugars as the alkali-soluble rice bran hemicelluloses did, but in different amounts. The predominant sugar for Starbonnet-La. and Tex. was arabinose, whereas glucose was predominant for Starbonnet-Ark. and Calrose. With the exception of Calrose, which had a ratio of arabinose to xylose of 1:1, those for the remaining Starbonnets were higher, ranging from 1.3 to 1.8:1, indicating a higher degree of branching. These ratios are much higher than those for the alkali-soluble bran hemicelluloses, but are considerably lower than that of the water-soluble endosperm hemicelluloses. The amounts of associated protein are similar to those found for the bran and ranged from 9.5% for Starbonnet-La. to 27.9% for Starbonnet-Ark. The hexuronic acid content of all four samples was 10%.

The composition of water-soluble rice endosperm hemicelluloses is shown in Table III. These rices also contained the same sugars found in previous samples but, unlike the others, glucose was predominant in all four samples analyzed. The arabinose and xylose contents are much lower than for the alkali-soluble hemicelluloses; however, the ratios of arabinose to xylose are much higher, ranging from 4:1 for the Starbonnet-La. to 7:1 for the Starbonnet-Tex. and the Calrose. It is interesting to note that the arabinose to galactose ratios for all of the water-soluble hemicelluloses are nearly constant. Perhaps the galactose in rice, like that in wheat, occurs as an arabinogalactan (Neukom and Markwalder, 1975; Fincher et al., 1974). The contents of the proteins associated with these polysaccharides are not uniform and are much lower than was those of the alkali-soluble hemicelluloses. Similarly, the hexuronic acid content is also lower than for the other samples. Although the arabinose, xylose, and galactose contents for Calrose are lower than those for Starbonnets, the ratios of both the arabinose–xylose and

Table IV. Amino Acids in Water-Soluble Rice Endosperm Hemicelluloses Weight Percent of Recovered Amino Acids

amino acid	rice variety Starbonnet La.	Starbonnet Ark.	Starbonnet Tex.	Calrose Cal.
Ala	9.4	8.0	9.5	7.9
Val	7.3	7.1	4.2	4.4
Gly	6.3	6.3	4.2	7.0
Ile	3.1	3.6	2.1	2.6
Leu	6.3	5.4	4.2	5.3
Pro	5.2	4.5	3.2	4.4
Thr	5.2	5.4	5.3	5.3
Ser	9.4	8.0	11.6	9.6
Met	1.0	1.0	1.1	0.4
Hypro	9.4	6.3	8.4	5.3
Phe	4.2	4.5	2.1	4.4
Asp	7.3	11.6	13.7	13.2
Glu	8.3	12.5	13.7	14.0
Tyr	3.1	4.5	3.2	4.4
Lys	4.2	6.3	4.2	6.1
His	3.1	1.8	6.3	1.8
Arg	7.3	3.6	4.2	3.5

Table V. Amino Acids in Alkali-Soluble Rice Bran Hemicelluloses Weight Percent of Recovered Amino Acids

amino acid	rice variety Starbonnet La.	Starbonnet Ark.	Starbonnet Tex.	Calrose Cal.
Ala	5.3	8.7	6.9	7.1
Val	4.7	5.1	5.1	5.6
Gly	5.6	6.3	6.3	6.1
Ile	3.0	3.0	3.4	3.8
Leu	7.0	9.0	8.8	9.3
Pro	5.3	7.5	6.4	7.3
Thr	3.3	3.6	3.4	4.5
Ser	5.0	5.7	5.4	5.5
Met	1.7	1.2	1.2	1.8
Hypro	0.7			0.5
Phe	6.0	6.0	5.8	6.0
Asp	12.3	14.7	14.1	13.8
Glu	22.3	11.4	13.9	11.6
Tyr	2.0	3.3	2.4	2.2
Lys	6.6	5.7	5.4	5.3
His	3.3	3.9	4.4	3.0
Arg	6.0	4.2	7.1	6.3

Table VI. Amino Acids in Alkali-Soluble, Rice Endosperm Hemicelluloses Weight Percent of Recovered Amino Acids

amino acid	rice variety: Starbonnet La.	Starbonnet Ark.	Starbonnet Tex.	Calrose Cal.
Ala	6.9	6.6	6.6	6.0
Val	5.3	6.8	6.1	6.3
Gly	6.3	6.1	5.5	6.3
Ile	2.9	3.9	2.9	3.8
Leu	6.9	7.6	7.4	6.6
Pro	4.8	4.7	4.0	4.7
Thr	3.4	3.9	3.2	3.4
Ser	5.6	5.3	5.3	4.7
Met	1.9	0.4	1.3	0.9
Hypro	1.1			0.3
Phe	4.8	4.5	4.2	4.1
Asp	13.0	12.9	14.2	14.7
Glu	21.2	21.1	22.2	23.8
Tyr	2.9	3.2	3.4	2.8
Lys	6.1	6.6	6.4	6.3
His	1.9	1.6	1.7	1.3
Arg	5.3	3.9	5.7	4.1

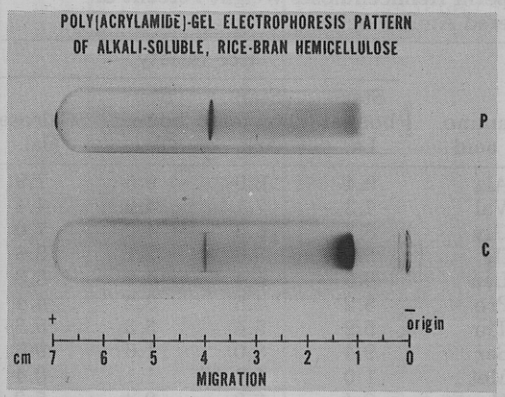

Figure 2. Polyacrylamide gel electrophoresis pattern of an alkali-soluble rice bran hemicellulose: C, carbohydrate; P, protein.

arabinose–galactose are about the same.

The amino acid composition of the protein associated with the water-soluble rice endosperm hemicellulose and the alkali-soluble bran and endosperm hemicelluloses is shown in Table IV, V, and VI, respectively. The amino acid patterns are not typical of those for plant storage proteins, as is illustrated by the low glutamic acid and arginine of all of the hemicelluloses and the significantly high hydroxyproline and serine of the water-soluble hemicelluloses.

The polyacrylamide gel electrophoresis pattern of an alkali-soluble rice bran hemicellulose, shown in Figure 2, indicates that two bands migrated during electrophoresis and both bands stained for carbohydrate (lower gel) and for protein (upper gel). The band near the origin is apparently a component of large molecular weight that consists predominately of carbohydrate, with less associated protein. The smaller band that migrated faster is apparently a component of smaller molecular weight that stains more heavily for protein, referred to by Yamagishi et al. (1975) as a proteoglycan hemicellulose. This evidence suggests that the proteins associated with the hemicelluloses are not contaminants, as previously reported (Gremli and Juliano, 1970) but are chemically bound to the carbohydrate moeity.

The crude (CF) and the neutral detergent fiber (NDF) contents of rice bran and endosperm are shown in Table VII. The results indicate an apparent greater difference between bran CF and NDF from California compared to bran CF and NDF of rice from the other growing areas than between CF and NDF of the varieties and of the endosperm. CF and NDF of bran from the long grain rice (Starbonnet) grown in Louisiana, Arkansas, and Texas were not strikingly different from those of the medium grain varieties (Nato and Brazos) grown in Texas. CF contents ranged from 9.2% for Louisiana-grown Starbonnet to 15.3% for Texas-grown Nato; NDF contents for these same two samples showed the same type differences. The greatest differences were observed for the Calrose medium grain rice. Both CF and NDF contents were significantly higher than those from the other long and medium grain rices in this study. These variations are present in the bran only. The endosperm CF and NDF for all varieties and growing areas showed little or no differences, suggesting that fiber composition of the rice bran only is affected by environmental conditions in the growing area and, to a lesser extent, by varietal differences.

Table VII. Crude and Neutral Detergent Fiber Contents of Rice Bran and Endosperm

variety	% bran: crude fiber	% bran: neutral detergent fiber	% endosperm: crude fiber	% endosperm: neutral detergent fiber
Starbonnet				
La.	9.2	29.7	0.3	2.9
Ark.	11.7	34.2	0.3	2.7
Tex.	10.3	29.8		
Calrose (Cal.)	21.1	44.7	0.3	2.4
Nato (Tex.)	15.3	33.0		
Brazos (Tex.)	11.5	28.7		

The quantitative and qualitative differences in sugars and amino acids of the rice hemicelluloses may be related to their interactions with other constituents during cooking, or with other metabolites during digestion and absorption after eating. Further studies are needed on their reactivity and the possible effect of hemicelluloses on cooking properties of rice.

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Instrumental Analysis of Volatiles from Rice and Corn Products

Michael G. Legendre, Harold P. Dupuy, Robert L. Ory,* and William O. McIlrath

Profiles of volatiles of whole rice, brown rice, polished rice, rice bran, rice breakfast cereal, whole corn, and corn breakfast cereal were obtained by direct gas chromatography without prior enrichment of volatiles. Some of the volatiles were identified by combined gas chromatography–mass spectrometry. Methanol, acetaldehyde, ethanol, acetone, pentanal, hexanal, and hexanol were found in volatiles of whole rice, brown rice, polished rice, rice bran, and whole corn. In addition, 2-methylpropanal, 2-methylpyrazine, furfural, 2,5-dimethylpyrazine, benzaldehyde, and 2,6-dibutyl-4-methylphenol were found in rice and corn breakfast cereals. This unconventional gas chromatographic technique in combination with mass spectrometry should provide a rapid means of analyzing volatiles that might impart desirable flavor or undesirable off-flavor in new cultivars and in raw and processed cereal products, before and after storage. Even at this early stage of development, the methodology is being used by industry to monitor raw materials.

In recent years, much research has been devoted to measurements of the flavor characteristics of rice, corn, and other foods. Relatively little work, however, has been done on these products in the raw state. Obata and Tanaka (1965) analyzed 50 g of polished rice and identified carbon dioxide, ammonia, hydrogen sulfide, and acetaldehyde. In 1966, Yatsumatsu et al. analyzed the volatile carbonyl compounds from 100 g of boiled rice and found that propanal (or acetone), pentanal, and hexanal seemed to be responsible for the stale flavor of cooked rice stored at elevated temperatures. Pyridine, hexanal, methylpropanal, and crotonaldehyde were reported by Inglett et al. (1968) as being among the flavor components they found in corn and corn products. Mitsuda et al. (1968) analyzed the volatiles from 3 kg of rice bran by gas chromatography (GC) and identified several compounds, among them methanol, ethanol, *n*-hexanol, acetaldehyde, acetone, methylpropanal, pentanal, and hexanal. Fifty grams of ground corn kernels were examined by Hougen et al. (1971), who found that different species and varieties of grain appeared to produce largely the same volatile components. Tsuzuki et al. (1975) analyzed the headspace gas from 20 g of cooked rice and found that the longer the cooking time, the more volatiles were produced. Bullard and Holguin (1977) analyzed the volatiles from 3 kg of unprocessed rice by combined capillary-column gas chromatography–mass spectrometry (GC–MS) and showed that the volatile flavor components of unprocessed rice are attractive to Philippine rice field rats.

Direct GC was used to analyze volatile flavor components from less than 1 g of raw and roasted peanut products (Brown et al., 1972; Fore et al., 1973) and of vegetable oils (Dupuy et al., 1971, 1976) and neutral volatiles in mayonnaise were examined and identified by direct GC–MS (Fore et al., 1976).

This paper presents the application of a direct, rapid, and simple GC–MS method for detecting and characterizing flavor-producing compounds in raw and processed rice and other cereal products. Less than 1 g of sample is used, without prior enrichment of volatiles.

MATERIALS AND METHODS

Materials. Standards used for determination of retention time and mass spectra were obtained from reliable sources. Silicone O-rings and poly-MPE (poly-*m*-phenoxylene) were purchased from Applied Science Laboratories, State College, Pa. (O-rings conditioned at 200 °C for 2 h). Pyrex glass wool was obtained from Corning Glass Works, Corning, N.Y. (conditioned at 200 °C for 16 h). Tenax-GC was obtained from TekLab., Inc., Baton Rouge, La., and Porapak P was obtained from Waters Associates, Framingham, Mass.

Gas Chromatography. The GC analyses were carried out on a Tracor MT-220 gas chromatograph with dual independent hydrogen flame detectors, a Westronics MT22 recorder, and a Hewlett-Packard 3380A integrator. The column used was $^1/_8$ in. by 9 ft stainless steel packed with 60/80 mesh Tenax-GC that had been coated with approximately (by weight) 7% poly-MPE (Novotny et al., 1975; Williams and Wille, 1976). The flow rate of the helium carrier gas was 40 mL/min. The inlet temperature was 120 °C, and the detector was kept at 250 °C. Hydrogen flow was 60 mL/min and air flow 470 mL/min.

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